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(54)【発明の名称】 黒色系酸化チタン粉末の製造方法

(57)【要約】

【構成】 二酸化チタン粉末と水素化ホウ素ナトリウムとの混合物を不活性ガス雰囲気下で300～950℃の温度で加熱することを特徴とする黒色系酸化チタン粉末の製造方法。

【効果】 還元性ガスを用いることなく低い還元処理温度で二酸化チタン粉末を加熱還元することにより混合性および分散性に優れた黒色酸化チタン粉末を安全に、低コストで製造することができる。

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【特許請求の範囲】

【請求項1】 二酸化チタン粉末と水素化ホウ素ナトリウムとの混合物を不活性ガス雰囲気下で300～950℃の温度で加熱することを特徴とする黒色系酸化チタン粉末の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は黒色系酸化チタン粉末の製造方法に関し、特に、水素化ホウ素ナトリウムを還元剤として用いる黒色系酸化チタン粉末の製造方法に関するものである。

【0002】

【従来の技術】従来より、黒色顔料としては、主に、カーボンブラックや四三酸化鉄が用いられてきた。

【0003】しかしながら、カーボンブラックは疎水性なので水に濡れにくい。また、一般に粒径が0.005 μm 程度と極端に小さい。したがって、他に汎用されている顔料、例えば、二酸化チタン粉末(粒径0.3 μm 程度)と混合して用いる場合に、配合比によって流動性が敏感に変化し、混合性に劣るという問題がある。また、カーボンブラックを工業的に生産する際には発癌性物質である3,4-ベンツピレンが混入する可能性があるので、安全性に問題がある。

【0004】一方、四三酸化鉄は磁化されやすく、比重は5.2と大きい。このため、顔料として用いた場合に、色分かれが生じたり、分散性に劣るなどの問題がある。また、大気中で150℃程度に加熱すると $\gamma\text{-Fe}_2\text{O}_3$ に変化し、変色するという問題もある。

【0005】このように、従来より使用されている黒色顔料には様々な問題点があり、より良好な混合性および分散性を有する品質の優れた黒色顔料が望まれている。そのような黒色顔料の一つに黒色系低次酸化チタン粉末がある。

【0006】黒色系低次酸化チタン化合物を得る方法としては、たとえば、特公昭52-12733号公報に開示されている二酸化チタン粉末と金属チタン粉末との混合物を真空または還元雰囲気中で550～1100℃で1～5時間加熱する方法が挙げられる。

【0007】しかしながら、この従来法で黒色度の高い酸化チタン化合物を得るためには、二酸化チタン粉末と金属チタン粉末との混合物を950～1,100℃の高温で加熱する工程を必要とする。二酸化チタン粉末をこのような高温で加熱すると粒子同士が焼結して粗大化する。したがって、従来の二酸化チタン還元法では混合性および分散性の良好な均一な粒径を有する黒色系酸化チタン粉末を得ることが困難である。

【0008】また、特開昭64-72921号公報および特開昭64-72922号公報には、二酸化チタン粉末を無水ヒドラジンガス等のような特殊雰囲気中で加熱還元する方法が開示されている。

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【0009】しかしながら、一般に、これらの還元性ガスは腐食性が強いので、取扱いおよび反応装置、設備等の面で種々の制約がある。

【0010】

【発明が解決しようとする課題】本発明は上記従来の問題を解決するものであり、その目的とするところは、還元性ガスを用いることなく低い還元処理温度で二酸化チタン粉末を加熱還元することにより混合性および分散性に優れた黒色系酸化チタン粉末を提供可能な、安全性が高く、低コストの黒色系酸化チタン粉末の製造方法を提供することにある。

【0011】

【課題を解決するための手段】本発明者らは、上記課題を解決するために鋭意研究の結果、不活性雰囲気下で300～950℃の温度で加熱すれば、上記目的が達成されることを見出し、本発明に到達した。すなわち、本発明は、二酸化チタン粉末と水素化ホウ素ナトリウムとの混合物を不活性雰囲気下で300～950℃の温度で加熱することを特徴とする黒色系酸化チタン粉末の製造方法を要旨とするものである。

【0012】本発明に用い得る二酸化チタン粉末としては、アナタース、ルチル、ブルッカイト型のいずれでもよい。粉末の粒子寸法は特に限定されないが、良好な混合性および分散性を有する黒色系酸化チタン粉末を得るためには粒径0.2 μm 以下の粉末であることが好ましい。このような二酸化チタン粉末は市販されており、例えば、和光純薬工業(株)社製の「試薬一級二酸化チタン」、テイカ(株)社製の「JR」および「JA-1」、およびフロイント産業(株)社製の「A-HR」および「R-SM3」が挙げられる。

【0013】本発明に用い得る水素化ホウ素ナトリウムとしては、98%以上の純度を有する粉末状水素化ホウ素ナトリウムであれば特に限定されない。水素化ホウ素ナトリウム粉末は、約250 μm 以下の粒径を有する微粉末であることが好ましい。粉末の粒径が小さい方が混合均一性および反応性が増すためである。このような水素化ホウ素ナトリウムは市販されており、例えば、(株)モートン・インターナショナル社製の「 NaBH_4 」、および川研ファインケミカル(株)社製の「 NaBH_4 」が挙げられる。

【0014】本発明では、まず、水素化ホウ素ナトリウム粉末と二酸化チタン粉末との混合物が調製される。水素化ホウ素ナトリウム粉末と二酸化チタン粉末との混合比はモル比で1:8～1:2の範囲とすることが好ましい。混合比が1:8以下になると還元能力が低下するので十分な黒色度が得られない。混合比が1:2以上になると黒色度は増すけれども製造コストが上昇する。

【0015】このような量の水素化ホウ素ナトリウム粉末および二酸化チタン粉末は、当業者に周知の方法により混合される。例えば、ロッキングミキサーで混合することにより本発明に用い得る水素化ホウ素ナトリウム粉

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末と二酸化チタン粉末との混合物が得られる。

【0016】得られた混合物は加熱用容器に投入される。本発明の加熱工程では特殊雰囲気が必要とせず加熱温度も低いことから、用いる加熱用容器に特に制約はなく、通常のステンレス鋼もしくはセラミックス製容器が用いられる。本発明の好ましい実施態様では、例えば、SUS-309S(日本ステンレス(株)社製)が用いられる。

【0017】次いで、加熱用容器内部に不活性ガスをパージすることにより、容器内部の空気が不活性ガスに置換される。本発明に用い得る不活性ガスには、例えば、窒素、アルゴンおよびヘリウム等が挙げられる。

【0018】次いで、加熱容器に密閉された上記混合物は300~950℃の範囲、好ましくは400~850℃の範囲の温度に加熱される。

【0019】加熱温度が300℃未満であると得られる酸化チタン色は灰色系となるので黒色顔料として好ましくない。これは、水素化ホウ素ナトリウムの分解温度が約300℃なので、300℃未満では二酸化チタン粉末の還元が十分進行しないためと考えられる。一方、950℃を超える温度に加熱した場合は、原料のチタン粉末が焼結することによる粒子の成長が生じる。したがって、分散性が良好な均一な粒子寸法を有する黒色系酸化チタン粉末が得られない。また、このような高温に加熱すると製造コストが上昇するという問題も生じる。

【0020】上記加熱工程では水素化ホウ素ナトリウムが分解することにより二酸化チタンの部分還元反応が生じる。加熱処理時間は、1~4時間程度が好ましい。したがって、本発明では、還元反応は比較的短時間のうちに進行する。

【0021】得られた粉末状生成物は不活性雰囲気中で50℃以下、好ましくは常温まで冷却され、次いで試料重量の約2倍量の水で洗浄、濾過、そして120℃で静置乾燥される。その後、乾式法または湿式法或いはこれらを組み合わせて粉砕が行われ、黒色系低次酸化チタン粉末が得られる。

【0022】本発明の方法では、従来の方法と比較して低温、且つ簡易な装置で黒色系酸化チタン粉末を製造可能である。さらに、加熱工程中の酸化チタン粒子同志の焼結が防止されるので、混合性および分散性が良好な均一な粒径を有する微細粉末状黒色系酸化チタンが得られる。

【0023】

【実施例】以下の実施例により本発明を更に具体的に説明する。

【0024】なお、色調については東京電色(株)社製全自動色差計カラーエースTC-8600Aを用いて粉末セル法によって測色を行い、ハンター表色系のL値を測定した。

【0025】また、生成粒径については日本電子(株)社製走査電子顕微鏡JSM-5200を用いて測定を行った。

【0026】

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【実施例1】水素化ホウ素ナトリウム粉末と平均粒径0.18μmの二酸化チタン粉末とをモル比で1:8の割合で均一に混合し、この混合物を窒素ガス気流中の不活性雰囲気中において、450℃で3時間加熱した。得られた粉末状生成物を同一雰囲気中で50℃まで冷却し、水洗、乾燥、粉砕を行った。得られた黒色系酸化チタン粉末のL値を表1に、平均粒径を表2に示す。

【0027】

【実施例2】水素化ホウ素ナトリウムと平均粒径0.18μmの二酸化チタン粉末とをモル比で1:4の割合で均一に混合し、この混合物を窒素ガス気流中の不活性雰囲気中において、450℃で3時間加熱した。得られた粉末状生成物を同一雰囲気中で50℃まで冷却し、水洗、乾燥、粉砕を行った。得られた黒色系酸化チタン粉末のL値を表1に、平均粒径を表2に示す。

【0028】

【実施例3】水素化ホウ素ナトリウムと平均粒径0.18μmの二酸化チタン粉末とをモル比で1:4の割合で均一に混合し、この混合物を窒素ガス気流中の不活性雰囲気中において、450℃で1時間加熱した。得られた粉末状生成物を同一雰囲気中で50℃まで冷却し、水洗、乾燥、粉砕を行った。得られた黒色系酸化チタン粉末のL値を表1に、平均粒径を表2に示す。

【0029】

【実施例4】水素化ホウ素ナトリウムと平均粒径0.18μmの二酸化チタン粉末とをモル比で1:4の割合で均一に混合し、この混合物を窒素ガス気流中の不活性雰囲気中において、600℃で3時間加熱した。得られた粉末状生成物を同一雰囲気中で50℃まで冷却し、水洗、乾燥、粉砕を行った。得られた黒色系酸化チタン粉末のL値を表1に、平均粒径を表2に示す。

【0030】

【比較例1】金属チタン粉末と平均粒径0.18μmの二酸化チタン粉末とをモル比で1:4の割合で均一に混合し、この混合物を窒素ガス気流中の不活性雰囲気中において、450℃で3時間加熱した。得られた粉末状生成物を同一雰囲気中で50℃まで冷却し、粉砕を行った。得られた黒色系酸化チタン粉末のL値を表1に、平均粒径を表2に示す。

【0031】

【比較例2】水素化ホウ素ナトリウムと平均粒径0.18μmの二酸化チタン粉末とをモル比で1:4の割合で均一に混合し、この混合物を窒素ガス気流中の不活性雰囲気中において、1000℃で1時間加熱した。得られた粉末状生成物を同一雰囲気中で50℃まで冷却し、水洗、乾燥、粉砕を行った。得られた黒色系酸化チタン粉末のL値を表1に、平均粒径を表2に示す。

【表1】色調(ハンター表色系L値)

試料	色調(L値)
実施例1	16

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実施例 2	13
実施例 3	15
実施例 4	13
比較例 1	67
比較例 2	12

【0032】表1において、L値は明度を表す数値で、数値が小さい方が黒いことを示す。実施例2と比較例1では、加熱条件が同じであるにもかかわらずL値の差が54も生じた。これは、実施例2では水素化ホウ素ナトリウムの作用により低温でも還元が進行したためである。

【0033】一方、実施例2のように水素化ホウ素ナトリウムの混合比が高く、なおかつ処理時間の長いものほど還元反応が進行し、L値が小さくなった。また、比較例2のように高温で処理を行うとL値は小さくなった。

【表2】平均粒径

試料	平均粒径(μm)
実施例 1	0.18
実施例 2	0.18
実施例 3	0.18
実施例 4	0.19
比較例 1	0.32
比較例 2	0.63

【0034】表1の結果より、実施例1～4で得られた黒色系酸化チタン粉末の平均粒径は原料として用いた二酸化チタン粉末の平均粒径と実質的に同一であることが

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わかる。したがって、本発明の加熱工程では粒子同士の焼結による粒子の粗大化が起こらなかったことが示された。

【0035】一方、比較例1で得られた黒色系酸化チタン粉末の平均粒径は $0.32\mu\text{m}$ であり増大していた。これは、還元剤として添加した金属チタン粉末の粒径が大きいことに起因していると考えられる。また、 1000°C で加熱処理した比較例2では平均粒径は $0.63\mu\text{m}$ と増大しており、明らかに粒子同士の焼結による粗大化が起こっている。

【0036】

【発明の効果】本発明によれば、還元性ガスを用いることなく低い還元処理温度で二酸化チタン粉末を加熱還元することにより混合性および分散性に優れる黒色酸化チタン粉末を安全に、低コストで製造することができる。

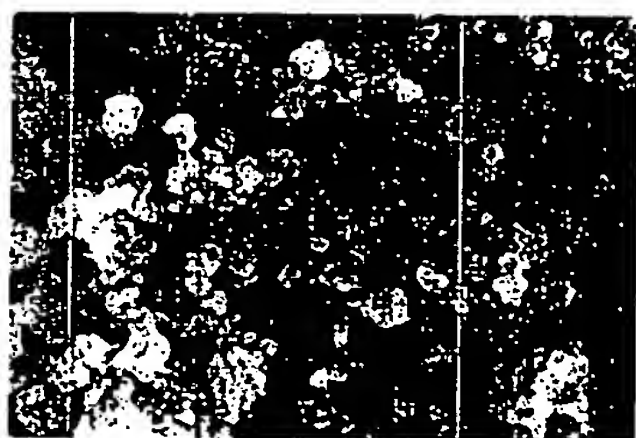
【図面の簡単な説明】

【図1】原料として用いた二酸化チタン粉末を20000倍の倍率で撮影した走査型電子顕微鏡写真である。

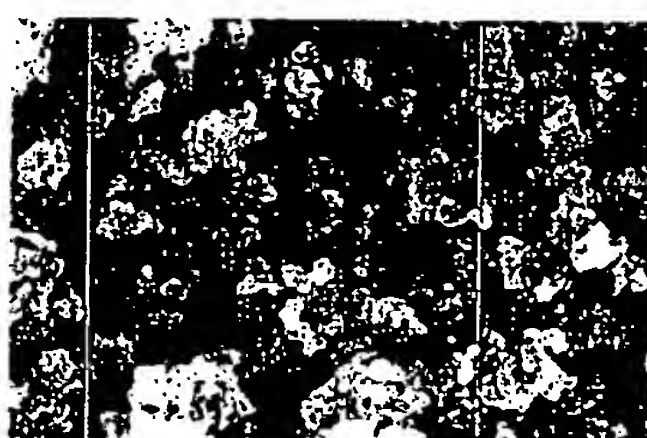
【図2】実施例1で得られた黒色系酸化チタン粉末を20000倍の倍率で撮影した走査型電子顕微鏡写真である。

【図3】比較例2で得られた黒色系酸化チタン粉末を20000倍の倍率で撮影した走査型電子顕微鏡写真である。

【図1】



【図2】



【図3】



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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the black system titanium oxide powder characterized by heating the mixture of titanium-dioxide powder and a sodium borohydride at the temperature of 300-950 degrees C under an inert gas ambient atmosphere.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] Especially this invention relates to the manufacture approach of the black system titanium oxide powder using a sodium borohydride as a reducing agent about the manufacture approach of black system titanium oxide powder.

[0002]

[Description of the Prior Art] Conventionally, as a black pigment, carbon black and a tri-iron tetraoxide have mainly been used.

[0003] However, since carbon black is hydrophobicity, it cannot get wet easily in water. Moreover, generally particle size is extremely as small as about 0.005 micrometers.

Therefore, when mixing with the pigment currently otherwise used widely, for example, titanium-dioxide powder, (particle size of about 0.3 micrometers) and using, there is a problem that a fluidity changes sensitively and is inferior to miscibility with a compounding ratio. Moreover, since the 3,4-Benzo-pyren which is a carcinogen may mix in case carbon black is produced industrially, a problem is in safety.

[0004] On the other hand, a tri-iron tetraoxide is easy to be magnetized, and specific gravity is as large as 5.2. For this reason, when it uses as a pigment, color separation arises or there are problems, such as being inferior to dispersibility. Moreover, when it heats at about 150 degrees C in atmospheric air, there is also a problem of changing and becoming gamma-Fe₂O₃.

[0005] Thus, there are various troubles in the black pigment currently used conventionally, and a black pigment which was excellent in the quality which has better miscibility and dispersibility is desired. Black system low hypo---ic acid-ized titanium powder is in one of such the black pigments.

[0006] The method of heating the mixture of the titanium-dioxide powder and titanium metal powder which are indicated by JP,52-12733,B at 550-1100 degrees C in a vacuum or reducing atmosphere as an approach of obtaining a black system low hypo---ic acid-ized titanium compound for 1 to 5 hours, for example is mentioned.

[0007] However, in order to obtain a high titanium oxide compound whenever black with

this conventional method, the process which heats the mixture of titanium-dioxide powder and titanium metal powder at a 950-1,100-degree C elevated temperature is needed. The grain children heated at such an elevated temperature sinter and make titanium-dioxide powder big and rough. Therefore, in the conventional titanium-dioxide reduction, it is difficult to obtain the black system titanium oxide powder which has a uniform particle size with good miscibility and dispersibility.

[0008] Moreover, the approach of carrying out heating reduction of the titanium-dioxide powder in special ambient atmospheres, such as anhydrous hydrazine gas, is indicated by JP,64-72921,A and JP,64-72922,A.

[0009] However, generally, since corrosive is strong as for these reducibility gas, it has constraint various in the field of handling and a reactor, a facility, etc.

[0010]

[Problem(s) to be Solved by the Invention] The place which this invention solves the above-mentioned conventional problem, and is made into the purpose has the high safety which can offer the black system titanium oxide powder which is excellent in miscibility and dispersibility by carrying out heating reduction of the titanium-dioxide powder at low reduction processing temperature, without using reducibility gas, and is to offer the manufacture approach of the black system titanium oxide powder of low cost.

[0011]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, when heating at the temperature of 300-950 degrees C under the inert atmosphere wholeheartedly as a result of research, this invention persons found out that the above-mentioned purpose was attained, and reached this invention. That is, this invention makes a summary the manufacture approach of the black system titanium oxide powder characterized by heating the mixture of titanium-dioxide powder and a sodium borohydride at the temperature of 300-950 degrees C under an inert atmosphere.

[0012] As titanium-dioxide powder which can be used for this invention, any of ANATASU, a rutile, and a BURUKKAITO mold are sufficient. Although especially a powdered particle dimension is not limited, in order to obtain the black system titanium oxide powder which has good miscibility and good dispersibility, it is desirable that it is powder with a particle size of 0.2 micrometers or less. Such titanium-dioxide powder is marketed, for example, "A-HR" and "R-SM3" by the "reagent first class titanium dioxide" by Wako Pure Chem Industrial company, and "JR", "JA-1" and Freund Industrial by TAYCA [CORP.] CORP. are mentioned.

[0013] It will not be limited especially if it is the powdered sodium borohydride which has 98% or more of purity as a sodium borohydride which can be used for this invention. As for sodium-borohydride powder, it is desirable that it is the impalpable powder which has the particle size of about 250 micrometers or less. It is for mixed homogeneity and reactivity of the one where a powdered particle size is smaller to increase. Such a sodium borohydride is marketed, for example, "NaBH₄" by Morton International company and

"NaBH₄" by Kawaken Fine Chemicals [Co., Ltd.] Co., Ltd. are mentioned.

[0014] In this invention, the mixture of sodium-borohydride powder and titanium-dioxide powder is prepared first. As for the mixing ratio of sodium-borohydride powder and titanium-dioxide powder, it is desirable to consider as the range of 1:8-1:2 by the mole ratio. Since reduction capacity will decline if a mixing ratio becomes 1:8 or less, whenever [sufficient / black] is not obtained. If a mixing ratio becomes 1:2 or more, although whenever [black] will increase, a manufacturing cost rises.

[0015] Such sodium-borohydride powder and titanium-dioxide powder of an amount are mixed by this contractor by the well-known approach. For example, the mixture of the sodium-borohydride powder and titanium-dioxide powder which can be used for this invention is obtained by mixing by the locking mixer.

[0016] The obtained mixture is fed into the container for heating. At the heating process of this invention, a special ambient atmosphere is not needed, but from also whenever [stoving temperature] being low, there is especially no constraint in the container for heating to be used, and usual stainless steel or the usual container made from the ceramics is used for it. In the desirable embodiment of this invention, SUS-309S (Nippon Stainless Steel [Co., Ltd.] Co., Ltd. make) are used, for example.

[0017] Subsequently, the air inside a container is permuted by inert gas by purging inert gas inside the container for heating. Nitrogen, an argon, helium, etc. are mentioned to the inert gas which can be used for this invention.

[0018] subsequently, the above-mentioned mixture sealed by the heating container -- the range of 300-950 degrees C -- it is preferably heated by the temperature of the range of 400-850 degrees C.

[0019] Since the titanium oxide color obtained as whenever [stoving temperature] is less than 300 degrees C serves as a gray system, it is not desirable as a black pigment. Since the decomposition temperature of a sodium borohydride is about 300 degrees C, this is considered for reduction of titanium-dioxide powder not to advance enough at less than 300 degrees C. On the other hand, when it heats to the temperature exceeding 950 degrees C, growth of the particle by the titanium powder of a raw material sintering arises. Therefore, the black system titanium oxide powder with which dispersibility has a good uniform particle dimension is not obtained. Moreover, if it heats to such an elevated temperature, the problem that a manufacturing cost rises will also be produced.

[0020] At the above-mentioned heating process, when a sodium borohydride decomposes, the partial reduction reaction of a titanium dioxide arises. The heating processing time has about 1 - 4 desirable hours. Therefore, in this invention, a reduction reaction advances to the inside of a short time comparatively.

[0021] It is preferably cooled by 50 degrees C or less to ordinary temperature in an inert atmosphere, and, subsequently standing desiccation of the obtained powdered product is carried out at washing, ***, and 120 degrees C with the water of the amount of about 2 times of sample weight. Then, grinding is performed combining dry process, a wet

method, or these, and black system low hypo---ic acid-ized titanium powder is obtained. [0022] In the approach of this invention, black system titanium oxide powder can be manufactured with low temperature and simple equipment as compared with the conventional approach. Furthermore, since sintering of the titanium oxide particle comrade in a heating process is prevented, the detailed powdered black system titanium oxide with which miscibility and dispersibility have a good uniform particle size is obtained.

[0023]

[Example] The following examples explain this invention still more concretely.

[0024] In addition, using full automatic color difference meter color ace TC[by Tokyo Denshoku / Co., Ltd. / Co., Ltd.]-8600A about a color tone, the colorimetry was performed by the powder cel method and L value of a hunter color coordinate system was measured.

[0025] moreover -- generation particle size -- the JEOL [Co., Ltd.] Co., Ltd. make -- it measured using scanning electron microscope JSM-5200.

[0026]

[Example 1] 1:8 came out comparatively by the mole ratio, sodium-borohydride powder and the titanium-dioxide powder of 0.18 micrometers of mean diameters were mixed uniformly, and this mixture was heated at 450 degrees C in the inert atmosphere in a nitrogen gas air current for 3 hours. The obtained powdered product was cooled to 50 degrees C in the same ambient atmosphere, and rinsing, desiccation, and grinding were performed. L value of the obtained black system titanium oxide powder is shown in Table 1, and mean particle diameter is shown in Table 2.

[0027]

[Example 2] 1:4 came out comparatively by the mole ratio, a sodium borohydride and the titanium-dioxide powder of 0.18 micrometers of mean diameters were mixed uniformly, and this mixture was heated at 450 degrees C in the inert atmosphere in a nitrogen gas air current for 3 hours. The obtained powdered product was cooled to 50 degrees C in the same ambient atmosphere, and rinsing, desiccation, and grinding were performed. L value of the obtained black system titanium oxide powder is shown in Table 1, and mean particle diameter is shown in Table 2.

[0028]

[Example 3] 1:4 came out comparatively by the mole ratio, a sodium borohydride and the titanium-dioxide powder of 0.18 micrometers of mean diameters were mixed uniformly, and this mixture was heated at 450 degrees C in the inert atmosphere in a nitrogen gas air current for 1 hour. The obtained powdered product was cooled to 50 degrees C in the same ambient atmosphere, and rinsing, desiccation, and grinding were performed. L value of the obtained black system titanium oxide powder is shown in Table 1, and mean particle diameter is shown in Table 2.

[0029]

[Example 4] 1:4 came out comparatively by the mole ratio, a sodium borohydride and the titanium-dioxide powder of 0.18 micrometers of mean diameters were mixed uniformly, and this mixture was heated at 600 degrees C in the inert atmosphere in a nitrogen gas air current for 3 hours. The obtained powdered product was cooled to 50 degrees C in the same ambient atmosphere, and rinsing, desiccation, and grinding were performed. L value of the obtained black system titanium oxide powder is shown in Table 1, and mean particle diameter is shown in Table 2.

[0030]
[The example 1 of a comparison] 1:4 came out comparatively by the mole ratio, titanium metal powder and the titanium-dioxide powder of 0.18 micrometers of mean diameters were mixed uniformly, and this mixture was heated at 450 degrees C in the inert atmosphere in a nitrogen gas air current for 3 hours. It ground by cooling the obtained powdered product to 50 degrees C in the same ambient atmosphere. L value of the obtained black system titanium oxide powder is shown in Table 1, and mean particle diameter is shown in Table 2.

[0031]
[The example 2 of a comparison] 1:4 came out comparatively by the mole ratio, a sodium borohydride and the titanium-dioxide powder of 0.18 micrometers of mean diameters were mixed uniformly, and this mixture was heated at 1000 degrees C in the inert atmosphere in a nitrogen gas air current for 1 hour. The obtained powdered product was cooled to 50 degrees C in the same ambient atmosphere, and rinsing, desiccation, and grinding were performed. L value of the obtained black system titanium oxide powder is shown in Table 1, and mean particle diameter is shown in Table 2.

[Table 1] Color tone (hunter color-coordinate-system L value) sample Color tone (L value) example 1 16 examples 2 13 examples 3 15 examples 4 Example 1 of 13 comparisons Example 2 of 67 comparisons 12 [0032] In Table 1, L value is a numeric value showing lightness, and it is shown that the one where a numeric value is smaller is black. In the example 2 and the example 1 of a comparison, although heating conditions were the same, the difference of L value produced 54. This is because reduction advanced also at low temperature according to an operation of a sodium borohydride in the example 2.

[0033] on the other hand -- an example 2 -- like -- the mixing ratio of a sodium borohydride -- high -- in addition -- and in the longer thing of the processing time, the reduction reaction advanced and L value became small. Moreover, L value became small when processed at the elevated temperature like the example 2 of a comparison.

[Table 2] Mean-particle-diameter sample Mean-particle-diameter (micrometer) example 1 0.18 examples 2 0.18 examples 3 0.18 examples 4 Example 1 of 0.19 comparisons Example 2 of 0.32 comparisons 0.63 [0034] The result of Table 1 shows [the mean diameter of the titanium-dioxide powder used as a raw material, and] that the mean diameter of the black system titanium oxide powder obtained in the examples 1-4 is

substantially the same. Therefore, it was shown by the heating process of this invention that big and rough-ization of the particle by sintering of particles did not take place. [0035] On the other hand, the mean particle diameter of the black system titanium oxide powder obtained in the example 1 of a comparison is 0.32 micrometers, and was increasing. This is considered to originate in the particle size of the titanium metal powder added as a reducing agent being large. Moreover, in the example 2 of a comparison heat-treated at 1000 degrees C, mean particle diameter is increasing with 0.63 micrometers, and big and rough-ization by sintering of particles has taken place clearly.

[0036]

[Effect of the Invention] According to this invention, the black titanium oxide powder which is excellent in miscibility and dispersibility can be safely manufactured by low cost by carrying out heating reduction of the titanium-dioxide powder at low reduction processing temperature, without using reducibility gas.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] In case this invention prepares for a counter the public lottery supplied to the selling agency of public lottery by consecutive numbers, it relates to the grouping approach of the public lottery which made it simpler to kick by the group at a rose from previous consecutive numbers about a double figures number tail for selling in individual parts.

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PRIOR ART

[Description of the Prior Art] the counter which deals with public lottery sale on a small scale conventionally -- setting -- each class from an agency -- the public lottery for sale supplied by consecutive numbers was prepared for selling in individual parts at grouping *****. Although there was no regulation special about this grouping, to the customer who purchases ten or more roses, the group number needed to be sold so that it might ignore and a single figure number tail might include ten kinds from 0 to 9, and since they were these preparation, it had hope that there should just be the simple grouping approach. In addition, a group number is disregarded also in this invention.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since this invention consists of the above configuration, and it
can prepare equally for a rose the public lottery supplied to the small-scale public lottery
selling agency with sufficient performance from consecutive numbers every 100 sheets at
grouping and a counter according to this, it is very convenient.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, at a small-scale counter, there was comparatively much selling in individual parts of a small sum, and in spite of having needed to perform grouping to a rose from consecutive numbers with sufficient performance equally, there was no special proposal about the technique which can be performed simple manually.

[0004] This invention is made in view of such a situation, the above-mentioned technical problem is canceled, and it aims familiar at offering the grouping approach of the public lottery which enabled it to prepare the public lottery for sale for a rose with sufficient performance equally at grouping and a counter using the classification board which can be supplied.

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MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, in case this invention prepares for a counter the public lottery supplied to the selling agency of public lottery by consecutive numbers, it is the approach of kicking a rose from previous consecutive numbers by the group about a double figures number tail to selling in individual parts, and is characterized by including the following procedures.

- (1) Extract 100 from 00 to 99 about the double figures number tail of the public lottery for sale supplied by consecutive numbers.
- (2) Classify to 10 sets, using ten from 0 to 9 of the single figure number tail which makes the double figures number tail common about that of the extracted public lottery of 100 sheets as 1 set.
- (3) Draw the circle of a path suitably on the classification board, and while giving the location number of 0 to 9 in the clockwise direction about each location which allots this periphery the 10th [about] grade, consider as a classification location.
- (4) Arrange ten sheets of the above-mentioned class unit in the above-mentioned classification location, and pile a list on the ascending order which begins from the figure whose single figure upper number tail of the 1st sheet is a location number in heaps.
- (5) It extracts one sheet at a time from a location number 0 in the clockwise direction, ends in the 1st ** by the extract of a location number 9, and may be one set for selling in individual parts.
- (6) Next, it extracts one sheet at a time from a location number 9 in the clockwise direction, ends in the 2nd ** by the extract of a location number 8, and may be one set for selling in individual parts.
- (7) About henceforth [3 **], repeat an extract in the clockwise direction, being able to shift the location number of extract initiation and termination every [1] in descending order, and consider as grouping ***** at new ten sets after the above (5).

[0006] Moreover, above-mentioned procedure (1) - (3) is made common, the list in the above-mentioned procedure (4) is made into descending order, an extract is repeated being able to shift the above-mentioned procedure (5) every [1] in ascending order after termination / recovery about the continuing above-mentioned procedure (6) and (7),

grouping is completed and a thing may be carried out.
[0007] From 0 of the above-mentioned location number to 9 shall be given in the counterclockwise direction, and it shall extract in the counterclockwise direction further again.

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EXAMPLE

[Example] One example of this invention is explained below with reference to an accompanying drawing. The sign of the following (1) in sentence - (7) is used for explanation of the above-mentioned procedure, and it is shown that they are the same contents.

[0009] If three approaches with the suitable grouping approach which embodied the summary of this invention (examples 1, 2, and 3) are explained in order First, 100 from 00 to 99 are extracted as a common procedure about the double figures number tail of the public lottery for sale supplied by consecutive numbers (procedure 1). It classifies to 10 sets, using ten from 0 to 9 of the single figure number tail which makes the double figures number tail common about that of the extracted public lottery of 100 sheets as 1 set (procedure 2).

[0010] (Example 1) As the example of the grouping approach is shown in drawing 1, the classification board is prepared and the circle of a path is suitably drawn on this board, and while giving the location number of 0 to 9 in the clockwise direction about each location which allots this periphery the 10th [about] grade, it considers as a classification location (procedure 3).

[0011] And ten sheets of a class unit are arranged in a classification location, and a list is piled on the ascending order which begins from the figure whose single figure upper number tail of the 1st sheet is a location number in heaps (procedure 4).

[0012] Here, the ascending order of a single figure number tail is that it serves as a list to the addition-direction of 0->9 even if the sequence of numbers of numbers 0-9 begins from which figure, and descending order is the reverse. That is, while it is cautious of the handling of 0 and regarding {0123456789}, {9012345678}, {5678901234}, etc. as ascending order, {9876543210}, {0987654321}, {5432109876}, etc. are regarded as descending order.

[0013] In the example of illustration, it is referred to as {00-01-02-03-04-05-06-07-08-09} from on the ascending order of a single figure tail, i.e., a pile, to 00->09 in the classification location 0 the double figures number tail. In addition, there is no constraint in the relation between **** of the double figures number tail, and a location number,

and about arrangement, it is arbitrary and good.

[0014] All the conditions piled on the arrangement and ascending order to each classification location in this example in heaps are summarized to below.

Classification location 0:00->09: Ascending order {00-01-02-03-04-05-06-07-08-09}

Classification location 1:31->30: Ascending order {31-32-33-34-35-36-37-38-39-30}

Classification location 2:62->61: Ascending order {62-63-64-65-66-67-68-69-60-61}

Classification location 3:93->92: Ascending order {93-94-95-96-97-98-99-90-91-92}

Classification location 4:14->13: Ascending order {14-15-16-17-18-19-10-11-12-13}

Classification location 5:45->44: Ascending order {45-46-47-48-49-40-41-42-43-44}

Classification location 6:76->75: Ascending order {76-77-78-79-70-71-72-73-74-75}

Classification location 7:27->26: Ascending order {27-28-29-20-21-22-23-24-25-26}

Classification location 8:58->57: Ascending order {58-59-50-51-52-53-54-55-56-57}

Classification location 9:89->88: Ascending order {89-80-81-82-83-84-85-86-87-88}

[0015] Then, it extracts one sheet at a time from a location number 0 in the clockwise direction, and ends in the 1st ** by the extract of a location number 9 (inside 0->1->2->3->4->5->6->7->8->9 of drawing), and parts for one-set grouping for selling in individual parts are collected (procedure 5). The double figures tails of ten roses (one set) of the public lottery extracted here are [00, 31, 62, 93, 14, 45, 76, 27, 58, 89].

[0016] Subsequently, it extracts one sheet at a time in the clockwise direction, and ends and collects from a location number 9 in the 2nd ** by the extract of a location number 8 (procedure 6). The double figures tails of ten roses (one set) of the public lottery extracted here are [80, 01, 32, 63, 94, 15, 46, 77, 28, 59].

[0017] About henceforth [3 **], an extract is repeated in the clockwise direction, being able to shift the location number of extract initiation and termination every [1] in descending order similarly, and grouping is completed with new ten sets collected for every ** (procedure 7).

[0018] All extract sets are shown collectively below.

The 1st **: Extract starting position number 0: [00, 31, 62, 93, 14, 45, 76, 27, 58, 89]
(****)

The 2nd **: Extract starting position number 9: [80, 01, 32, 63, 94, 15, 46, 77, 28, 59]
(****)

The 3rd **: Extract starting position number 8: [50, 81, 02, 33, 64, 95, 16, 47, 78, 29]

The 4th **: Extract starting position number 7: [20, 51, 82, 03, 34, 65, 96, 17, 48, 79]

The 5th **: Extract starting position number 6: [70, 21, 52, 83, 04, 35, 66, 97, 18, 49]

The 6th **: Extract starting position number 5: [40, 71, 22, 53, 84, 05, 36, 67, 98, 19]

The 7th **: Extract starting position number 4: [10, 41, 72, 23, 54, 85, 06, 37, 68, 99]

The 8th **: Extract starting position number 3: [90, 11, 42, 73, 24, 55, 86, 07, 38, 69]

The 9th **: Extract starting position number 2: [60, 91, 12, 43, 74, 25, 56, 87, 08, 39]

The 10th **: Extract starting position number 1: [30, 61, 92, 13, 44, 75, 26, 57, 88, 09]

[0019] (Example 2) As other examples are shown in drawing 2, the same classification

board as the above is prepared, and the classification location which gave the same location number is prepared.

[0020] And arrange ten sheets of a class unit in a classification location, and a list is piled on the descending order which begins from the figure whose single figure upper number tail of the 1st sheet is a location number in heaps. It extracts one sheet at a time from a location number 0 in the clockwise direction, and ends in the 1st ** by the extract of a location number 9 (inside 0->1->2->3->4->5->6->7->8->9 of drawing), and parts for one-set grouping for selling in individual parts are collected (procedure 5).

[0021] That is, the pile in this case is as follows.

Classification location 0:00->01: Descending order {00-09-08-07-06-05-04-03-02-01}

Classification location 1:31->32: Descending order {31-30-39-38-37-36-35-34-33-32}

Classification location 2:62->63: Descending order {62-61-60-69-68-67-66-65-64-63}

Classification location 3:93->94: Descending order {93-92-91-90-99-98-97-96-95-94}

Classification location 4:14->15: Descending order {14-13-12-11-10-19-18-17-16-15}

Classification location 5:45->46: Descending order {45-44-43-42-41-40-49-48-47-46}

Classification location 6:76->77: Descending order {76-75-74-73-72-71-70-79-78-77}

Classification location 7:27->28: Descending order {27-26-25-24-23-22-21-20-29-28}

Classification location 8:58->59: Descending order {58-57-56-55-54-53-52-51-50-59}

Classification location 9:89->80: Descending order {89-88-87-86-85-84-83-82-81-80}

In addition, there is no constraint in the relation between **** of the double figures number tail, and a location number, and arbitrary and good one is the same about arrangement.

[0022] Then, henceforth [2 **] repeats an extract, being able to shift every [1] in ascending order about the above-mentioned procedure (6) and (7), and completes grouping.

[0023] All extract sets are shown collectively below. In addition, the same set as the example of grouping of an example 1 is obtained also in this case.

The 1st **: Extract starting position number 0: [00, 31, 62, 93, 14, 45, 76, 27, 58, 89] (****)

The 2nd **: Extract starting position number 9: [80, 01, 32, 63, 94, 15, 46, 77, 28, 59]

The 3rd **: Extract starting position number 8: [50, 81, 02, 33, 64, 95, 16, 47, 78, 29]

The 4th **: Extract starting position number 7: [20, 51, 82, 03, 34, 65, 96, 17, 48, 79]

The 5th **: Extract starting position number 6: [70, 21, 52, 83, 04, 35, 66, 97, 18, 49]

The 6th **: Extract starting position number 5: [40, 71, 22, 53, 84, 05, 36, 67, 98, 19]

The 7th **: Extract starting position number 4: [10, 41, 72, 23, 54, 85, 06, 37, 68, 99]

The 8th **: Extract starting position number 3: [90, 11, 42, 73, 24, 55, 86, 07, 38, 69]

The 9th **: Extract starting position number 2: [60, 91, 12, 43, 74, 25, 56, 87, 08, 39]

The 10th **: Extract starting position number 1: [30, 61, 92, 13, 44, 75, 26, 57, 88, 09]

[0024] (Example 3) As the example of further others is shown in drawing 3, the same classification board as the above is prepared, it arranges in procession, and a location

number is given.

[0025] Also in this case, ten sheets of a class unit are arranged in the number location (classification location) of 0-9. And a list is piled on the ascending order or descending order which begins from the figure whose single figure upper number tail of the 1st sheet is a location number in heaps. It extracts one sheet at a time from a location number 0 in the clockwise direction, and ends in the 1st ** by the extract of a location number 9 (inside 0->1->2->3->4->5->6->7->8->9 of drawing), and parts for one-set grouping for selling in individual parts are collected (procedure 5).

[0026] And when it piles on ascending order in heaps, it extracts according to the above-mentioned example 1, and henceforth [2 **] is extracted according to the above-mentioned example 2, when it piles on descending order in heaps. (Procedures 6 and 7)

[0027] If three approaches mentioned above are the suitable examples seen from the point of simplicity and the grouping approach of this invention is summarized about these, it can be said that it is not necessary arrange, make order and the order of an extract into a summary, and to adhere to especially the layout of a classification location the location number of the classification location arranged in early stages, and there.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is an explanatory view at the time of piling on the ascending order which is one example of this invention in heaps.

[Drawing 2] It is an explanatory view at the time of piling on the descending order which is other examples of this invention in heaps.

[Drawing 3] It is an explanatory view at the time of changing into a matrix the arrangement (classification location) by the classification board which are other examples of this invention.

[Description of Notations]

1 Classification Board

2 Public Lottery

[Translation done.]